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13. ABSTRACT (*Maximum 200 words*)

Epitaxial Si films doped with high concentrations (10^{19} cm^{-3}) of the rare earth element Er have been deposited. The deposition technique used was low temperature plasma enhanced chemical vapor deposition with an electron cyclotron resonance source. The deposition temperatures were below 500 °C to avoid formation of erbium silicide which is optically inactive. The growth process for undoped samples was developed to the point that good quality epitaxial material could be obtained on demand. Some work was done investigating the concept of limited epitaxial thickness.

Four different metal organic Er precursors were tried and the greatest success was found with tris (bis trimethyl silyl amido) Er (III). A designed experiment was performed to determine the most important process conditions required to maximize the photoluminescence emission. Reasonably intense photoluminescence emission has been obtained, camparable to the level obtained by other groups, yet no absolute intesity calibration is currently available. Chemical analysis of the films was performed with both SIMS and RBS. The films do contain some carbon contamination, but the current thinking that this acts to reduce the lattice constant in the vicinity of the optical center and reduces the creation of crystalline defects.

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Final Technical Report to the

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

concerning the

LOW TEMPERATURE EPITAXIAL GROWTH OF RARE EARTH DOPED SILICON AND SILICON GERMANIUM ALLOYS

Grant Numbers F49620-92-J-0484

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A. Publications

1. J. L. Rogers, W. J. Varhue and E. Adams, "Growth of Er Doped Si Films by ECR Plasma Enhanced Chemical Vapor Deposition", Rare Earth Doped Semiconductors, Ed. by P. Klein and G. Pomrenke, Mater. Res. Soc. Vol. 130, San Fransisco, (1993).

2. J. L. Rogers, W. J. Varhue, E. Adams, M. A. Lavoie and R. O. Frenette, "Growth of Er Doped Si Films by ECR Plasma Enhanced Chemical Vapor Deposition", J. of Vac. Sci. and Technol., A 12(5) 2762 Sept. (1994).

3. J. L. Rogers, P. Andry, W. J. Varhue, P. McGaughnea, Ed Adams, R. Contra, "Low temperature homoepitaxial growth of Si by ECR-PECVD", Appl. Phys. Lett., 67 (7) 1995.

4. J. L. Rogers, P. S. Andry, W. J. Varhue, E. Adams, M. Lavoie and P. B. Klein, "Erbium Doped Silicon Films Grown by Plasma Enhanced Chemical Vapor Deposition", Journal of Applied Physics (in Press).

5. W. J. Varhue, J. L. Rogers, P. Andry, and E. Adams, "Epitaxial film thickness in the low temperature growth of Si(100) by plasma enhanced chemical vapor deposition", Appl. Phys. Lett. 68 (3) 349 (1996).

6. P. Andry, J. L. Rogers, W. J. Varhue, E. Adams, M. Lavoie, P. Klein, R. Hengehold, and J. Hunter, "Growth of Er-doped Si using Metal Organic Dopant Sources", Presentation at the American Vacuum Society in Minneapolis. (Oct 1995).

7. P. S. Andry, W. J. Varhue, F. G. Anderson, E. Adams, M. Lavoie, P.B. Klien, R. Hengehold and J. Hunter, "Low Temperature Growth of Si:Er by Electron Cyclotron Resonance PECVD Using Metalorganics", Mater. Res. Soc. , San Fransisco, (1996). (in press)

8. P. S. Andry, W. J. Varhue, F. Ladipo, K. Ahmed, E. Adams, M. Lavoie, P.B. Klien, R. Hengehold and J. Hunter, " Growth of Er-doped Si using Metalorganics by Plasma Enhanced Chemical Vapor Deposition", J. of Applied Physics, to be pulished July 1996.

9. W. J. Varhue, J. L. Rogers, P. S. Andry, E. Adams, M. Lavoie and R. Kontra, "Low Temperature Deposition of Epitaxial Si", Solid State Tech. , June (1996)

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C. Introduction

This document is the final technical report on the growth of rare earth doped Si under Award #F49620-92-J-0484. The concept of Er doped semiconductors is a relatively new and exciting prospect in the field of optoelectronics. If a large concentration Er or other rare earth element can be used to successfully dope Si, the potential for near term electrically pumped lasers and optical amplifiers will be greatly increased. This would open up an entirely new field, silicon light emitters for Si based devices. The goal of this investigation has been to develop a commercially compatible technique to deposit thick, high concentration, precipitation free, rare earth doped Si films. The low temperature growth technique used was plasma enhanced chemical vapor deposition with an electron cyclotron resonance(ECR) source. Low temperature processing (<500 ^{o}C) is needed to avoid the formation of $ErSi_2$ precipitates which are known to be optically inactive.

In the initial stages of this investigation, it became apparent that the epitaxial quality of the Si films that were deposited in our process were inadequate. The material suffered from a high concentration of unwanted impurities as well as a large density of crystalline defects. The poor epitaxial film quality was not sufficient to support efficient luminescence of incorporated optically active Er centers. Further it appeared that there was a limiting epitaxial film thickness, that is films that began growing epitaxially, would go amorphous after some characteristic thickness was reached. Therefore it was determined that some effort should be invested at the beginning of this investigation into understanding the growth process of Si at low substrate temperatures. This effort eventually resulted in the publication of three papers, listed above, as well as the establishment of a well defined process which permits easy growth of high quality epitaxial Si films at low substrate temperature, less than 500 ^{o}C.

The bulk of the overall project concentrated on doping the epitaxial films with optically active erbium centers. In the later stages of this investigation, effort has been spent on refining the deposition process as well as trying a series of post deposition processes to maximize the luminescent output. We believe that our laboratory currently produces material with the most efficient photoluminescence emission for Si:Er materials codoped with C, N or O. The research highlights resulting from work over the past three years will be described below.

Research

1. Growth of Si Thin Films:

The first samples prepared in this investigation were of low quality, containing metallic impurities such as Fe and Ni and possessing a high density of crystalline defects. The determination of film quality was made principally by Rutherford Backscatter Spectrometry. The metallic impurities were determined to result from ion sputtering occurring from the reactor's resonance chamber walls. A sketch of the reactor design can be found in figure 1.0. The problem of ion

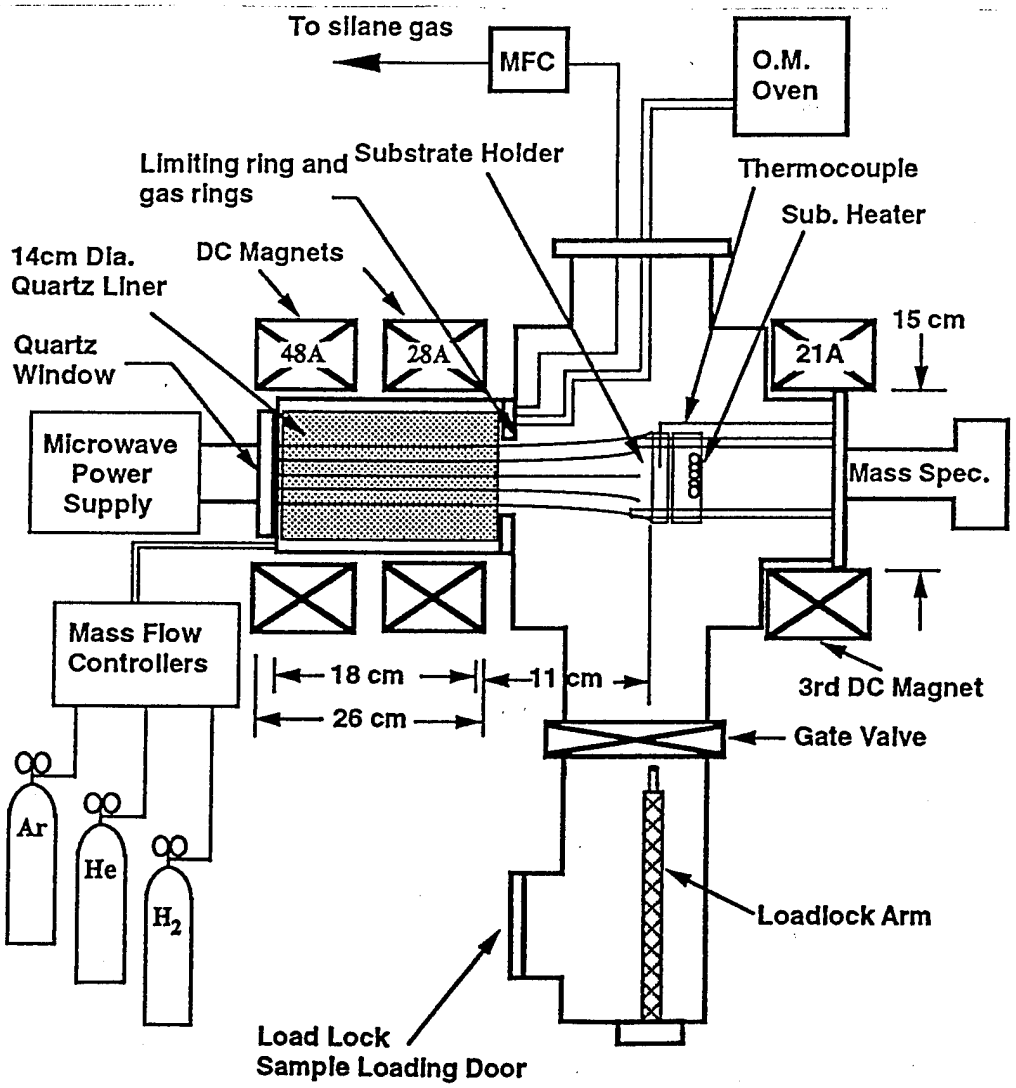


Figure 1. Electron cyclotron resonance reactor.

sputtering was solved through a change in the magnetic field profile, figure 2, as well as the inclusion of a limiting ring separating the resonance chamber from the deposition chamber. An additional measure involved the addition of a quartz liner in the resonance chamber. This reduced the plasma potential in the resonance chamber and reduced the energy of ions impinging on the chamber walls. Initially we experimented with using different inert gas combinations in the resonance chamber to form the ECR discharge as there was no consences from the literature. Unexpectedly it was found that using mixtures of inert gases in the discharge region resulted in high energy ions which increased the observed sputtering problem. Because of difficulties encountered in obtaining a stable He plasma, a pure Ar plasma was finally chosen. With these changes the incorporation of metallic impurities into the deposited films was eliminated.

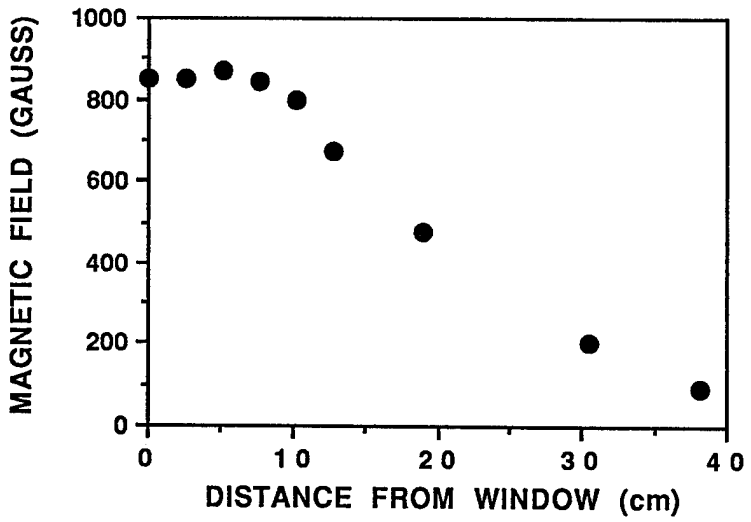


Figure 2. Magnetic field profile in ECR chamber.

The large density of defect sites however was still a major puzzle. At that time in the investigation there were published reports by K. Fukuda et. al.(1) of obtaining epitaxial Si growth at a substrate temperature of 200 °C in a similar ECR process. Repeated attempts to repeat these results appeared to fail. Actually the film thicknesses obtained in the Fukuda study were actually quite small, on the order of a few hundred Å, whereas we were attempting to grow a few thousand Å. Our investigation eventually moved to higher substrate temperatures, in the range of 400 to 500 °C, and epitaxy was achieved. The dependence of epitaxial thickness on substrate temperature appeared to be a new phenomenon. The current

thinking at the time was that there was a critical substrate temperature required for epitaxial growth. For the sake of the overall intention to incorporate Er without silicide formation, the lowest possible growth temperature was attractive. Several films were grown with varying substrate temperature and their epitaxial thicknesses were measured by RBS. A plot of the limited epitaxial thickness as a function of substrate temperature is shown in figure 3.

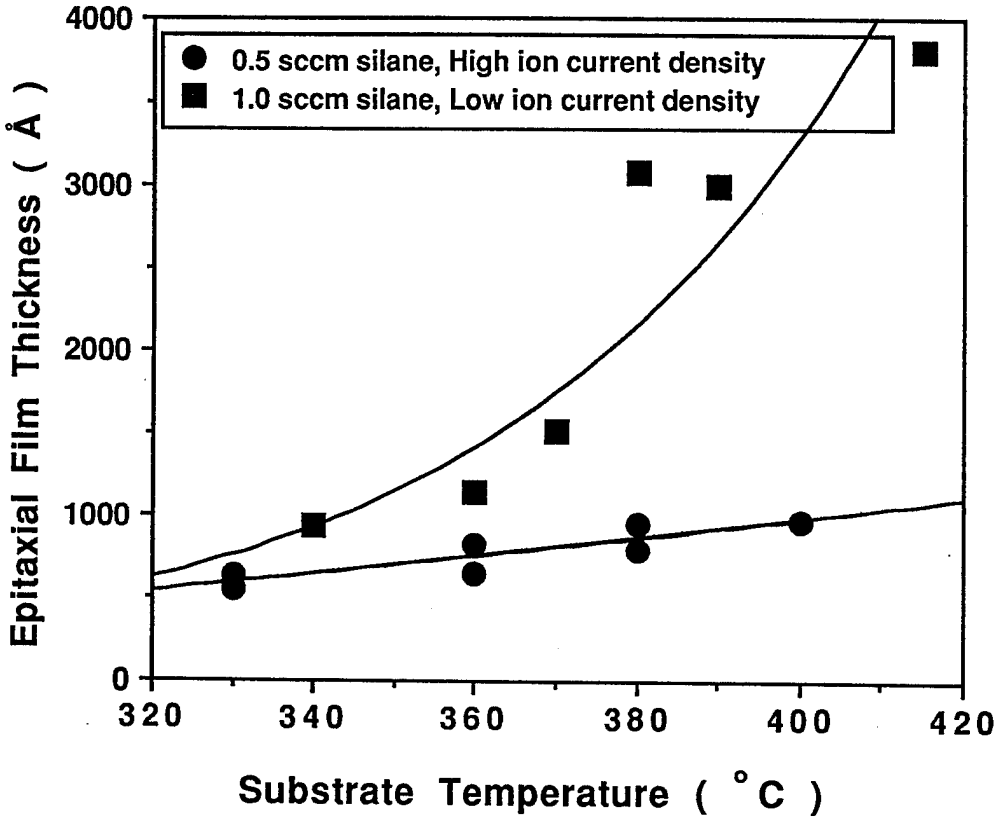


Figure 3. Limited epitaxial thickness as a function of substrate temperature for two different levels of energetic ion bombardment.

Clearly the limited epitaxial thickness increases with substrate temperature. The two curves on this plot represent a difference in the amount of energetic ion bombardment per Si adatom. The lower ion bombardment case represents an ion flux level of 135 ions/adatom with an average ion energy of 13 eV. The higher case represents a flux ratio of approximately 300 ions/adatom with the same average ion energy. The level of ion bombardment per adatom in the present system was varied by the strength of the axial magnetic field in the vicinity of the substrate region or the

microwave power level delivered to the discharge or the feed rate of silane to the reactor. A more direct comparison of epitaxial thickness and ion current density can be seen in figure 4. An interesting result

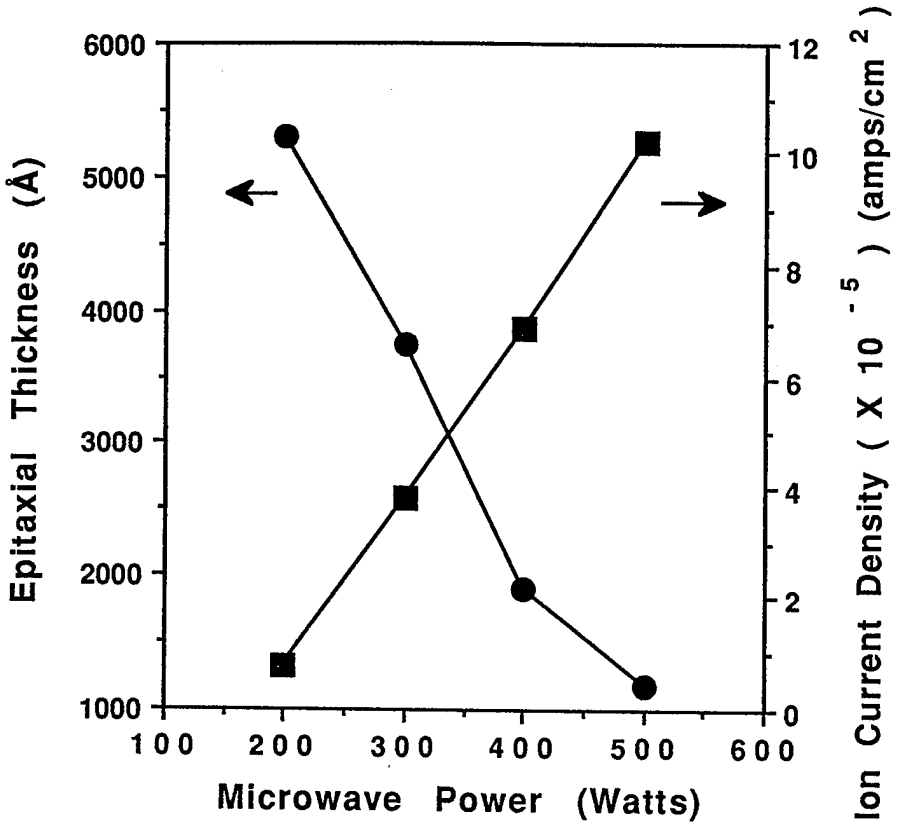


Figure 4. Dependence of epitaxial thickness and ion current density with microwave power level.

of this investigation was a comparison of these results with two other investigations performed using MBE(2 and 3), figure 5. As can be seen in this figure there is little difference between the values for the limited epitaxial thickness by the two techniques despite the significant difference occurring in the two processes.

We have continued this work in some respects to consider the effect of hydrogen in the process. A comparison was made of films deposited by the typical silane PECVD process and those deposited with Si atoms sputtered from tagets in the deposition chamber. Epitaxial films were obtained with the sputtered Si sources, but the limited epitaxial thickness was less than half of the silane grown thickness. This suggests that hydrogen is acting as a surfactant in the deposition process with silane. Mixing the chemical and

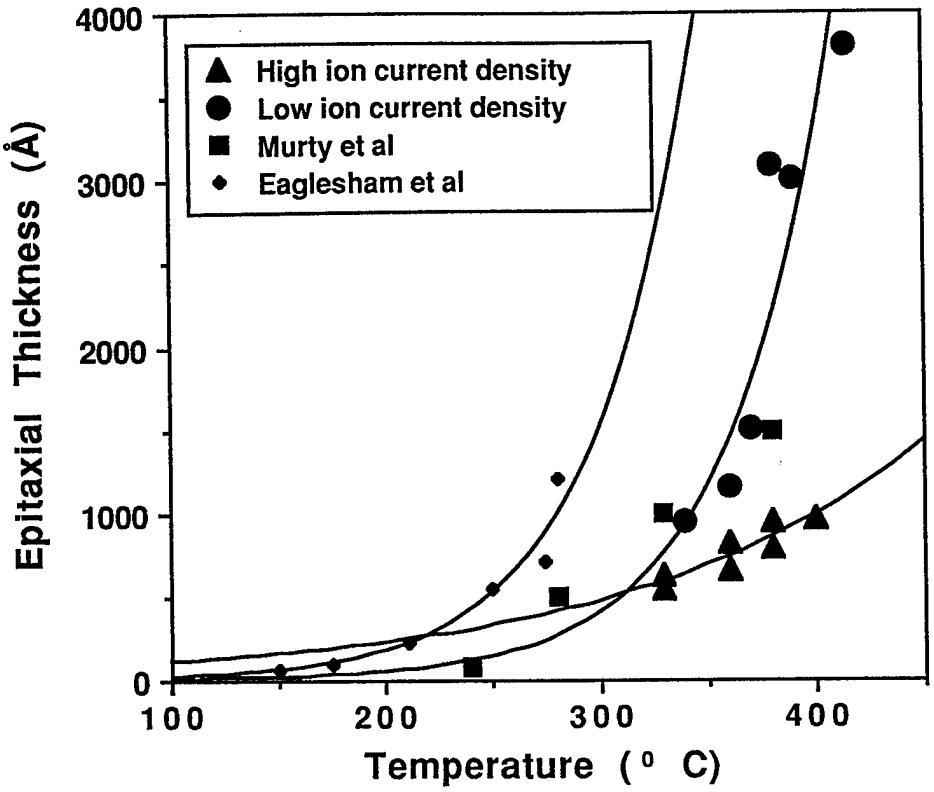


Figure 5. A comparison of limited epitaxial thickness from two previous investigations using MBE and this investigation using PECVD.

sputtered Si sources resulted in a total loss of epitaxy. This indicates that the sputtered Si atoms disturbs the surfactant balance found with the gas source growth and results in nucleation of the amorphous phase. The deliberate addition of hydrogen to the growth with silane was found to delay the transition to the amorphous phase by better than a factor of two. However, the addition of hydrogen was not able to maintain film quality as the concentration of stacking faults increased with films thickness. The effect of hydrogen addition may also be to chemically etch surface protrusions which typically nucleate amorphous phase growth.

Although more work could be done exploring the low temperature deposition of silicon in this process regime, we concluded that we had developed a reliable process for depositing good quality epitaxial films in a temperature range from 375 to 500 °C.

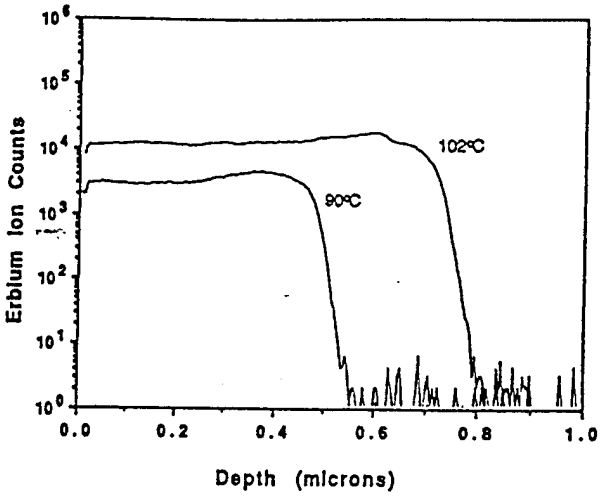
The specific deposition conditions are as follows:

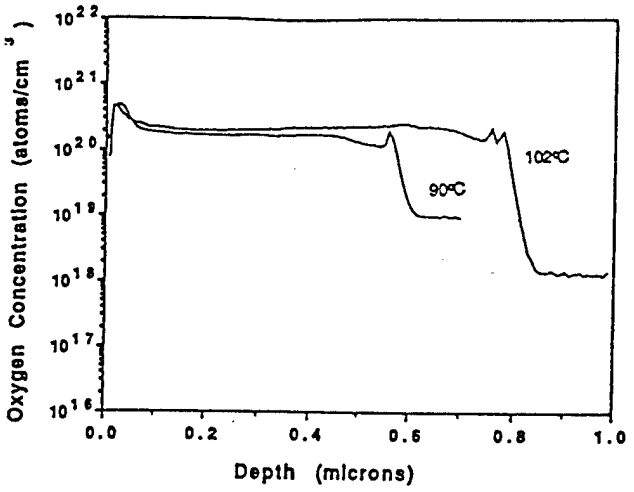
Substrate temperature	375 to 500 oC
Reactor Pressure	5 mtorr
Silane flow rate (downstream)	1 to 2 sccm
Argon flow rate(upstream)	40 sccm
Microwave power level	200 Watts
Film thickness	1000 to 4000 Å
Clean Process	
Ex-situ	Degrease in TCA
	Rinse in methanol
	Rinse in DI water
	HF dip
	Rinse in DI water
	Blow dry
In-situ	Ar/H plasma
	Duration: 1 min.
	Pressure 5 mTorr
	Power 200 Watts
	Flow Rate 10 H_2/40 Ar

Other changes that were made and used to improve the deposition process included covering the microwave window with an alumina cover plate. This was later changed to an alumina coating obtained by spray pyrolysis directly onto the quartz window. This was found to significantly reduce to oxygen content of the Si films. A technique which also reduced the oxygen content of the deposited material was to perform a five minute Ar purge of the system immediately before the in-situ clean cycle was initiated. A plot showing Secondary Mass Spectroscopy (SIMS) results for thisprocess can be found in figure 6.

2. Er Doped Si:

We have deposited a large number of samples using four different metal organic (MO) compounds under a variety of process conditions. All compounds were solid sources which were sublimed into the reactor from a heated source and delivery tube. The first compound tried was (2,2,6,6)-tetramethyl-3,5-heptanedionato erbium, abbreviated $Er(thd)_3$. The molecular structure of this compound is shown in figure 7. It was possible to vary the concentration of Er in the film from 10^{17} to 10^{19} per cm^{-3} by controlling the source temperature, figure 8. It was found however





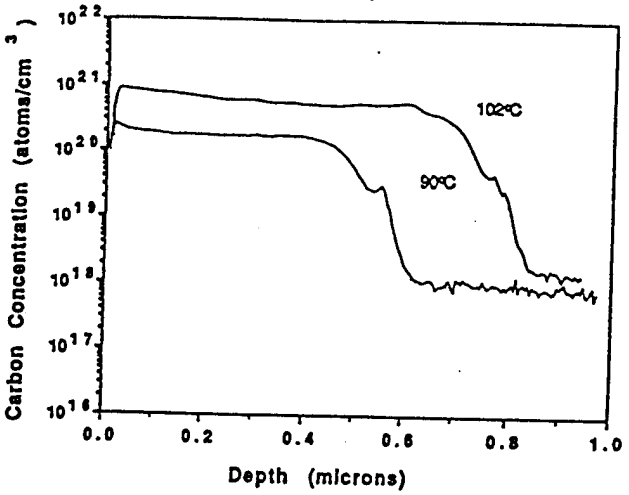
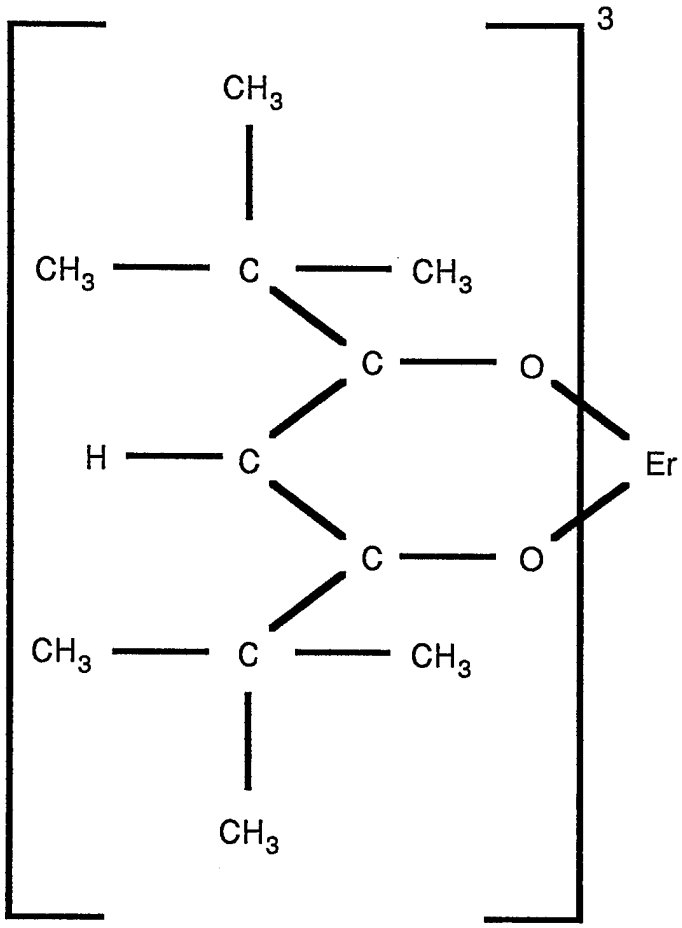


Figure 6. Secondary ion mass spectrometry results for two samples prepared with two different MO source temperatures.

TTHD Er Metalorganic



$Er(C_{11}H_{19}O_2)_3$

- Melting Point = 168-171°C
- Boiling Point = 290°C
- Atomic Weight = 717.08 AMU

Figure 7. Solid line structure diagram of the metalorganic molecule Tris(2,2,6,6-tetramethyl-3-5-heptanedionato)erbium(III).

that an increase in Er concentration to greater than 10^{19} cm^{-3} resulted in a decrease in crystal quality as shown by the "Chi Min" value, which is the ratio of channeled backscatter intensity to random backscatter intensity. A plot of the "Chi Min" value as a function of Er atom concentration is shown in figure 9. The most significant reason determined for the loss in crystal quality was actually the incorporation of carbon resulting from the disintegration

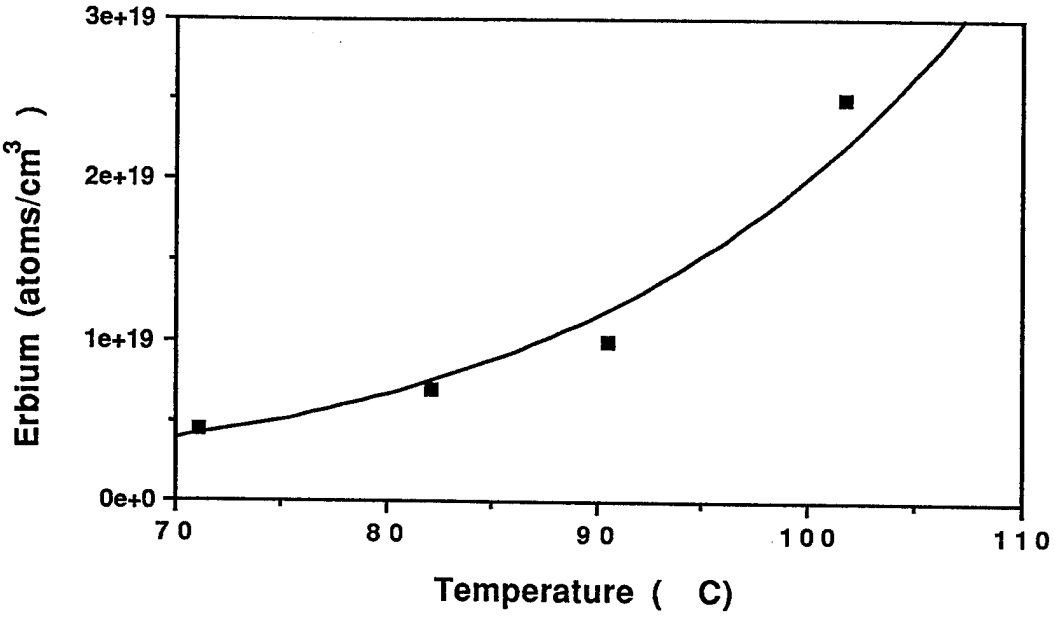


Figure 8. Erbium concentration in the films as a function of metal organic source temperature.

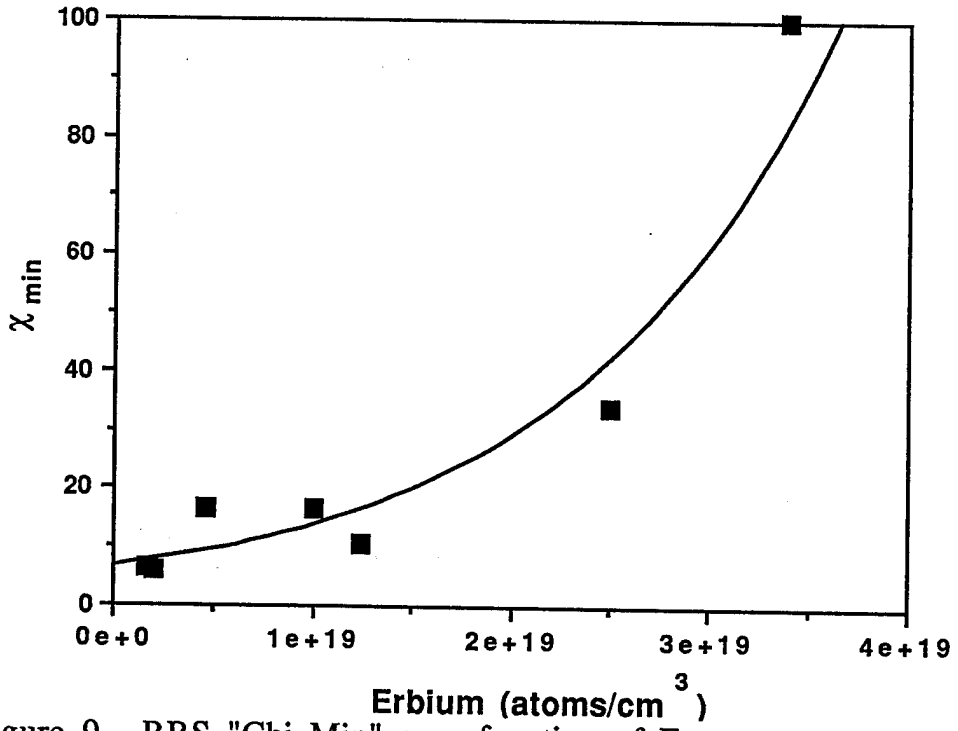


Figure 9. RBS "Chi Min" as a function of Er atom concentration in the film.

of the MO compound. The $Er(thd)_3$ compound contains 33 C atoms per Er atom. Chemical analysis of the deposited film with SIMS revealed that the films contained 33 C per Er atom. It appeared that the MO compound was not performing as planned, and that the organic ligands were decomposing on the wafer surface, and becoming incorporated into the growing film. Analysis of the film revealed an O content even higher than that anticipated from decomposition of the MO compound. This result lead to an examination of the microwave window and eventual to a modification of the window to include an alumina cover to prevent H reduction of the quartz. The samples deposited using this MO dopant source were sent to Dr. Paul Klien at NRL for photoluminescence characterization. A plot of the emission from three unannealed samples is shown in figure 10.

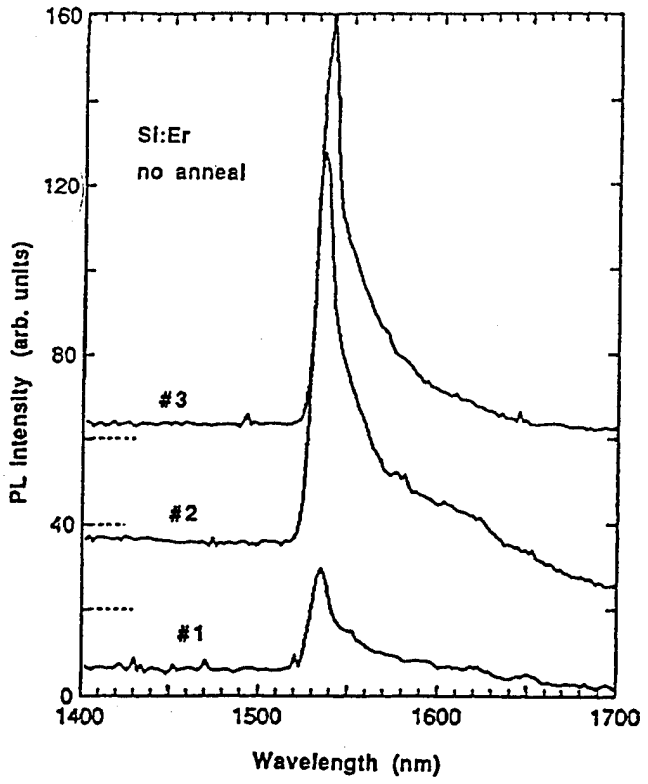
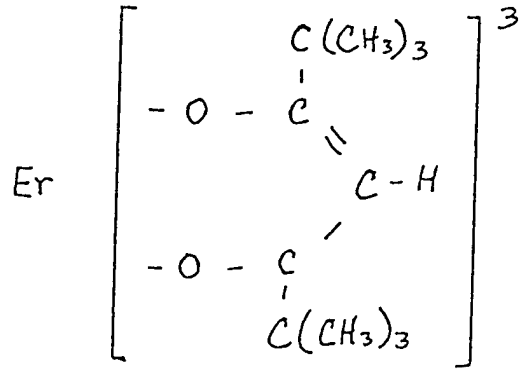


Figure 10. Photoluminescence spectrums of Er doped Si films grown at various MO source temperatures.

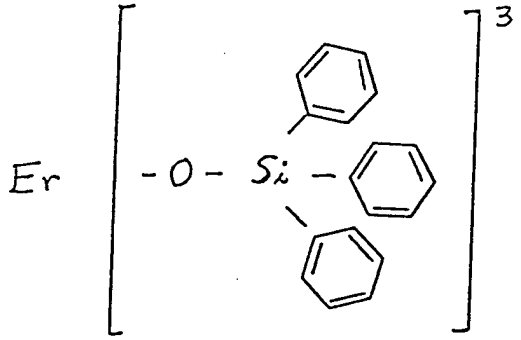
At that point in the investigation it was felt that the problem with excessive carbon contamination was seriously limiting material quality and ultimately photoluminescence output. The MO source that was currently in use was clearly vulnerable to disintegration and was the major source of excess carbon contamination. The research direction was enlargered to include a search for a more suitable MO coumpound which could more effectively deliver the optically active Er center, intact, without the large concentration of carbon impurities. Through the support a second AFOSR Contract, F49620-94-1-0427, our research group was enlarged to include a metal organic chemist, Dr. Kazi Ahmed at UVM. Dr. Ahmed synthesized a number of MO Er compounds for our use. A table showing the molecular structure of two of these compounds is shown in figure 11. None of these compounds proved to be a successful precursor for doping optically active Er centers in Si. The compounds were mainly unstable and disintegrated in the source bottle, leaving the Er atoms in a nonvolatile form.

The last compound tried, tris (bis trimethyl silyl amido) erbium, ("amido") shown in comparison to the first MO compound tried in figure 12, has resulted in significant success and has caused us to spend the majority of our time investigating its use. A comparison of the previous strongest luminescence result using the $Er(thd)_3$ precursor and now the amido compound prepared under similar conditions is shown in figure 13. Use of the "amido" compound results in an immediate increase in photoluminescence intensity of a factor of 8 for similar, unoptimized growth conditions. A factorial design experiment was performed to optimize the deposition conditions for use of the "amido" compound. The deposition conditions that were varied included; MO source temperature, silane flow rate, hydrogen flow rate, and growth time. Hydrogen addition was found to be strongly detrimental to luminescence efficiency, and it was proposed that H attacks the Er-N bond and thus destroys the optical activity of the Er center. Unexpectedly the two most significant deposition factors governing emission intensity were growth rate(silane flow rate) and overall growth time(overall sample thickness). A plot of the response surface is shown in figure 14. It appears that these two factors govern the chemical composition of the film which has a strong influence on the material's crystal structure. The use of the "amido" compound did not totally eliminate the C contamination problem, but did lessen it. More significantly, results from high resolution x-ray diffraction measurements indicate that in the "amido" case, C atoms are incorporated into the Si lattice structure and cause the x-ray peak to shift slightly to a shorter

1. [Tris (2,2,6,6-tetramethyl -3,5-heptanedionato) erbium (III)]



2. [Tris-(triphenyl-siloxy) erbium (III)]
*vapor pressure too low to be practical



3. [Tris-(triphenyl-carboxy) erbium (III)]

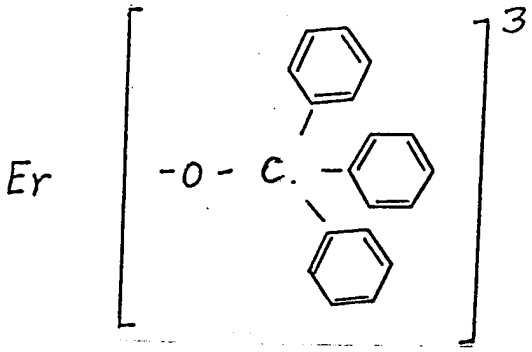


Figure 11. The molecular structure of three metal organic Er precursors used in this investigation. 1) shown for comparison was the first compound tried and was purchased from Strem Chemical., 2) and 3) were synthesized at the University of Vermont by Dr. Kazi Ahmed.

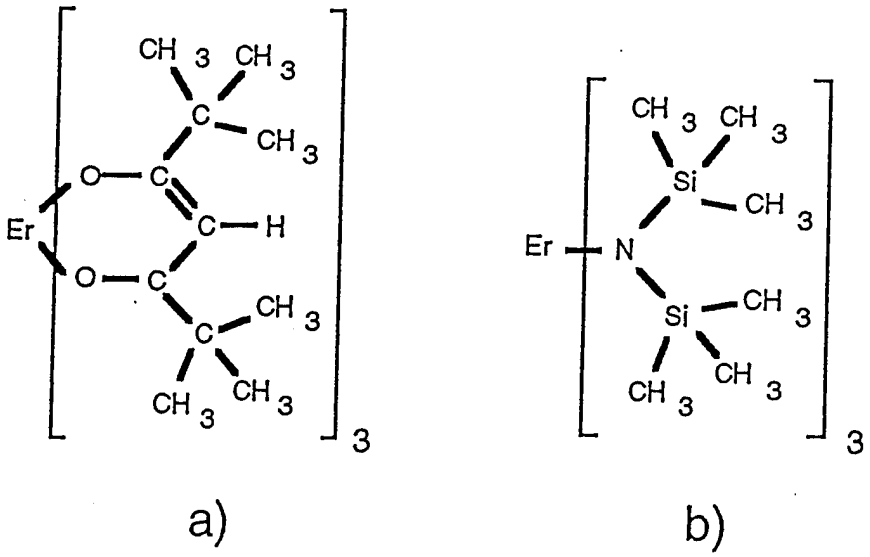


Figure 12. Molecular structure of MO dopants, a) tris (2,2,6,6-tetramethyl-3-5-heptanedionato) Er (III) and b) tris (bis trimethyl silyl amido) Er (III)

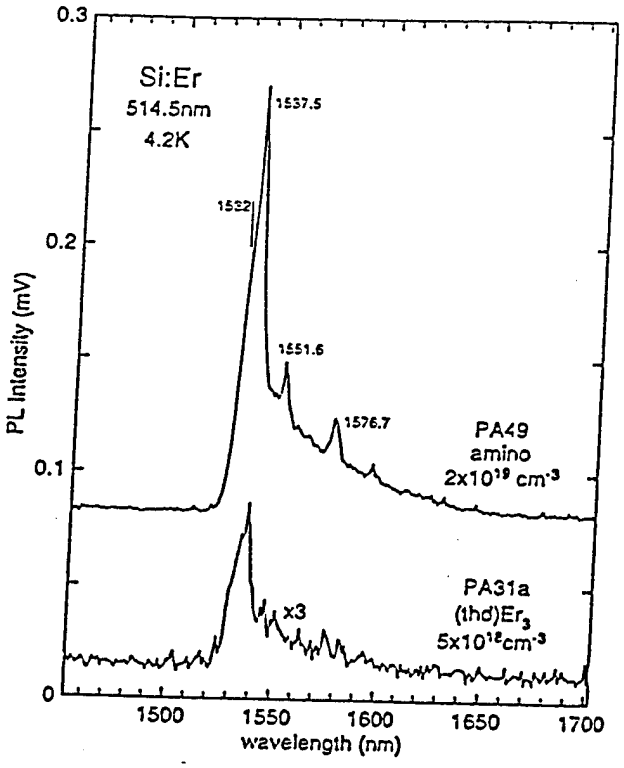


Figure 13. Comparison of PL intensity for two Er doped samples, #49 grown using the "amido" compound and #31 the best result using the $(thd)Er_3$ compound.

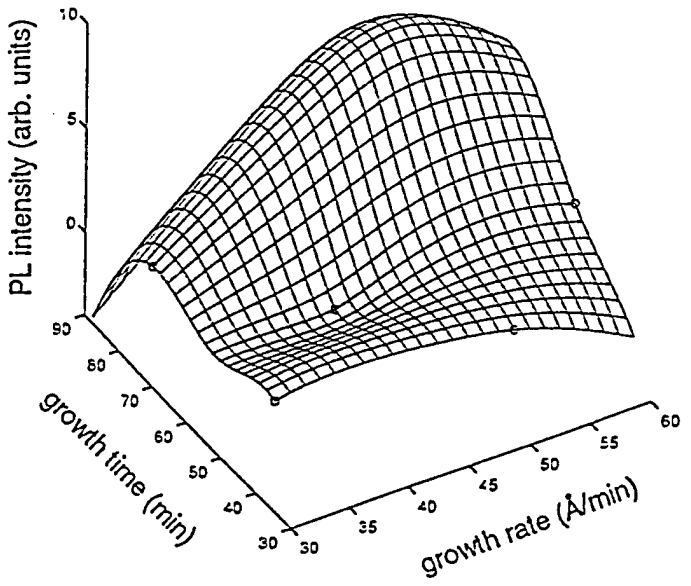


Figure 14. A plot of the PL response surface as a function of growth rate and growth time.

lattice constant proportional to its composition. The shift in lattice constant is not likely a factor in increasing luminescence intensity but rather the effect that it has in reducing the density of defects resulting from the incorporation of the larger Er optical centers. The current best photoluminescence spectrum that we have obtained from our unannealed material is shown in figure 15. The clarity of the secondary peaks in this spectra were sufficient to assist F.G.Anderson at UVM to propose a quantum mechanical model for the transitions appearing in the fine structure.[2]

Currently we are continuing efforts to perfect the deposition process and also making plans to construct a simple LED device. We do have some preliminary results on the effect of rapidly annealing of samples to increase emission intensity. Shown in figure 16 is a comparison of a sample as grown, and that following a 5 minute, 600 ^{o}C rapid thermal anneal step. The as grown sample was also sent to MIT for photoluminescence analysis, and was found to be equal to about 25 % the intensity of their best O codoped sample.

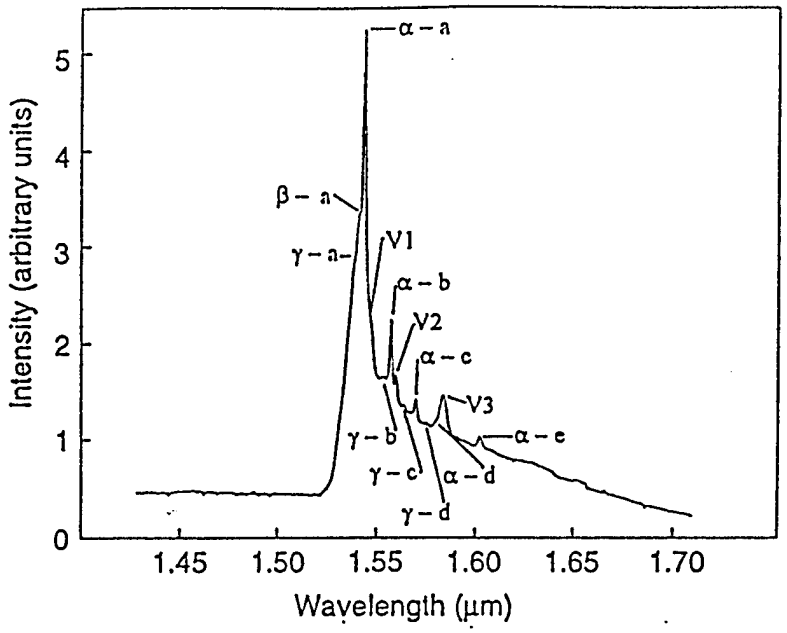


Figure 15. Current best photoluminescence spectrum from unannealed sample showing fine line structure.

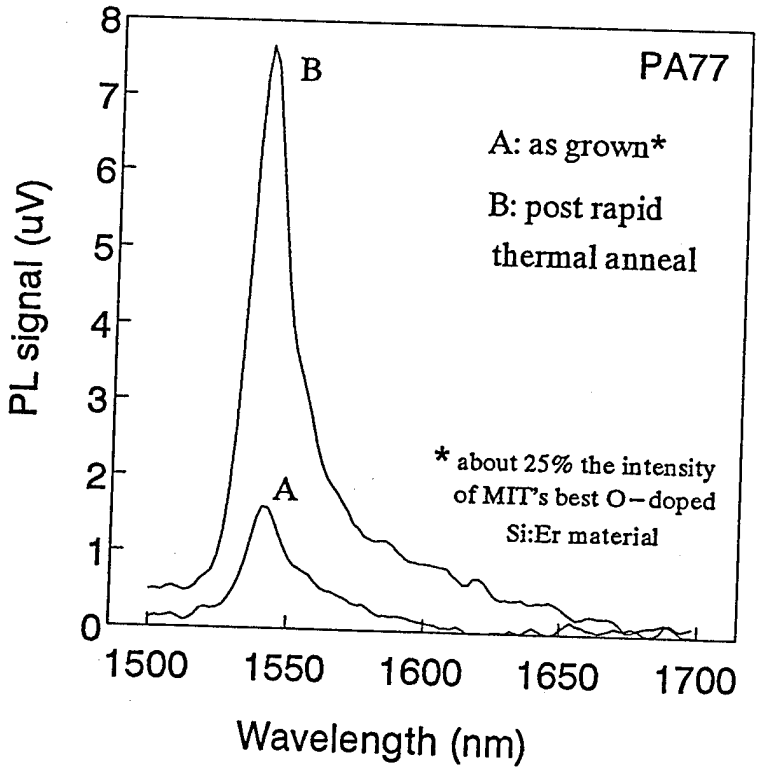


Figure 16. Comparison of photoluminescence spectrum for a sample as grown, and that following a 5 minute, 600 °C rapid thermal anneal step.

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